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Glycerol: Production, consumption, prices, characterization and new trends in combustion

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ABSTRACT

The demand for petroleum has been rising rapidly due to increasing industrialization and modernization. This economic development has led to a huge demand for energy, most of which is derived from fossil fuel. However, the limited reserve of fossil fuel has led many researchers to look for alternative fuels which can be produced from renewable feedstock. Increasing fossil fuel prices have prompted the global oil industry to look at biodiesel, which is from renewable energy sources. Biodiesel is produced from animal fats and vegetable oils and has become more attractive because it is more environmentally friendly and is obtained from renewable sources. Glycerol is the main by-product of biodiesel production; about 10% of the weight of biodiesel is generated in glycerol. The large amount of glycerol generated may become an environmental problem, since it cannot be disposed of in the environment. In this paper, an attempt has been made to review the different approaches and techniques used to produce glycerol (hydrolysis, transesterification, refining crude glycerol). The world biodiesel/glycerol production and consumption market, the current world glycerin and glycerol prices as well as the news trends for the use of glycerol mainly in Brazil market are analyzed. The technological production and physicochemical properties of glycerol are described, as is the characterization of crude glycerol obtained from different seed oil feedstock. Finally, a simple way to use glycerol in large amounts is combustion, which is an advantageous method as it does not require any purification. However, the combustion process of crude glycerol is not easy and there are technological difficulties. The news and mainly research about the combustion of glycerol was also addressed in this review.

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1. Introduction

Biofuels arose as a sustainable source of fuel in the search for new energy resources and are considered an important form of technological progress in limiting greenhouse gas emissions and diminishing pollution, improving air quality [1]. Biofuels are a source of renewable energy; they are produced from natural material (biologically based). Among the most common biofuels is ethanol generated from maize, wheat or beets and biodiesel from oily seeds and/or animal fat [2]. At present, biofuels are used as a source of energy as a substitute for fossil fuels because they are biodegradable, much cleaner and generate an acceptable level of emissions gases [3,4].

Biodiesel stands out among biofuels. It is a liquid fuel that's obtained from natural lipids such as vegetable oil or animal fat using industrial processes of esterification or transesterification. Biodiesel is superior to diesel oil for health and the environment (it is low in sulfur, emits a low level of noxious particles like HC and CO, and is better in the CO_2 cycle in reducing global warming), as well as for engine performance (better lubrication, high cetane number and more complete combustion) [5–7]. Biodiesel is biodegradable, renewable and non-toxic. It has a high flash point, better viscosity and caloric power similar to fossil fuels [7]. These advantages have convinced Asian countries to utilize biodiesel as an alternative fuel as one of the innovative solutions to reduce global air pollution generated by the growing number of vehicles [8]. Mixtures are the most viable way to increase biodiesel usage, elevating biodiesel's share of the fuel market, benefitting producers, guaranteeing competitive pricing for end users, and requiring less incentives and tax exemptions [9]. It has been reported that from 75 to 95% of the end price of biodiesel is influenced by the cost of the raw material [10].

On the other hand, production of biodiesel has a by-product: glycerol. Generally, 10 to 20% of the total volume of biodiesel produced is made up of glycerol [11–15]. The production of bioethanol also generates glycerol as a by-product, up to 10% of the weight of the sugar consumed [16]. Lately an intense debate has focused on this important problem in biodiesel production: the inevitable production of glycerol as a by-product with a low commercial value [12,17]. Growing biodiesel production will lead to large surpluses of glycerol. A fundamental question soon arises: What can be done with the glycerol? This is one of the main reasons that research at present is focused on developing technology to convert or use the glycerol in order to improve the biodiesel business and drastically improve its economic viability [12,18]. Though glycerol is a raw material and there are over 2000 industrial uses, incessant biodiesel production is leading glycerol to be dealt with as a waste product. Specific concerns about the social and environmental impacts of biodiesel production have been growing [19,20].

This manuscript is a review of the different approaches and techniques used to produce glycerol (hydrolysis, transesterification, refining crude glycerol), the world biodiesel/glycerol production and consumption market, the current world glycerin and glycerol prices and the news trends for the use of glycerol mainly in Brazil. Though it is not an ideal fuel, one option (other than its use in the pharmaceutical or chemical industries) could be to burn it (glycerol combustion) locally in a combined heat and energy generation process (cogeneration), replacing fossil fuels, and optimizing the efficiency of the process as well as reducing the impacts of this byproduct. The news and mainly research about the combustion of glycerol was also investigated in this review.

2. Glycerol

Glycerol is the main component of triglycerides, found in animal fat, vegetable oil, or crude oil. Glycerol is derived from soap or from biodiesel production [18,21]. It's been known since 2800 BCE, when it was isolated by heating fat mixed with ashes to produce soap [22]. However, it is considered to have been discovered in 1779 by Swiss pharmacist K. W. Scheele, who was the first to isolate this compound when he heated a mixture of litharge (PbO) with olive oil. In 1811, French chemist M. E. Chevrel called glycerin a liquid, defining the chemical formulas of fatty acids and the formulas of glycerin in vegetable oil and animal fat. His work was patented. It was known as the first industrial method to obtain glycerin soap by reacting fatty material with lime and alkaline material [23].

2.1. Glycerol's physical properties

Glycerol is the simplest of the alcohols and is known by propane-1,2,3-triol according to IUPAC. It is also commercially known as glycerin, 1,2,3-propanotriol, trihydroxypropane, glyceritol or glycidic alcohol [24]. Glycerol is an oily liquid; it is viscous, odorless, colorless, and has a syrupy-sweet taste. Glycerol is a liquid containing three hydrophilic hydroxyl groups that are responsible for it being hygroscopic and its solubility in water [25,26]. Fig. 1 shows the molecular structure of glycerol, made up of three hydroxyls.

Glycerin is completely miscible in many substances. Among them are: alcohol (methyl, ethyl, isopropyl, *n*-butyl, isobutyl, secondary butyl, and tertiary amyl); ethylene glycol, propylene glycol, trimethylene glycol monomethyl ether and phenol [28,29]. Solubility of glycerin in acetone is 5% by weight; in ethyl acetate it's 9%. It's slightly soluble in dioxane and ethyl, and partially insoluble in superior alcohol, fatty acids and hydrocarbonate, as well as in chlorinated solvents such as hexane, benzene, and chloroform. Glycerin is very viscous: at normal temperatures it remains a viscous liquid even at 100% concentration without crystallizing. At low temperatures, concentrated glycerin solutions tend to super cool as high viscosity fluid. Viscosity rises at first until it quickly becomes vitreous around −89 °C. Aqueous glycerin solutions (at different concentrations) tend to have lower viscosity [30].

At low temperatures glycerin tends to super cool instead of crystallize. Aqueous glycerin solutions resist freezing and are used as antifreeze in cooling systems. Glycerin does not oxidize in the atmosphere in normal conditions, but can be easily oxidized by other oxidants. Glycerin solutions need inhibitors when they are exposed to heat and in contact with ferrous metal or copper since the salts contained in these materials can catalyze oxidation [31]. Glycerol has low volatility and low vapor pressure, which is strictly linked with its hygroscopic property. Between 0 and 70 °C, temperature changes have little effect on the vapor pressure of glycerin solutions. Like other alcohols, glycerin has a lower vapor

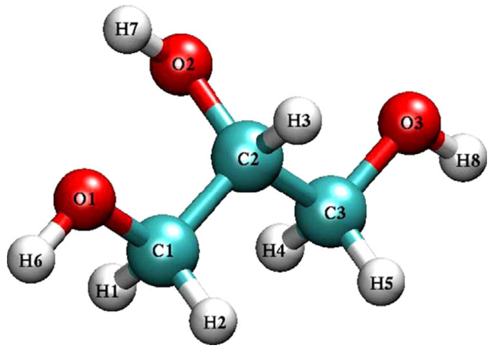


Fig. 1. Molecular structure of glycerol [27].

Table 1
Physical and chemical properties of glycerol.

Properties	Unit	Morrison [38]	Pagliaro and Rossi [39]	OECD-SIDS [40]
Molecular formula			$C_3H_5(OH)_3$	$C_3H_8O_3$
Molar mass	g/mol	92.09	92.09382	92
Relative density	kg/m^3	1260	1261	1260
Viscosity	Pa s	1.41	1.5	1.41
Melting point	°C	18	18.2	18
Boiling point (101.3 kPa)	°C	290	290	290
Flash point	°C	177	160 (closed cup)	160
Specific heat	kJ/kg	2435 (25 °C)		
Heat of vaporization	kJ/k-mol	82.12		
Thermal conductivity	W/(m K)	0.28		
Heat of formation	kJ/mol	667.8		
Surface tension	mN/m	63.4	64.0	63.4
pH (solution)		7		
Auto flammability	°C			393

Table 2
Analysis of three glycerol fuels [44].

	USP Glycerol	**Methylated**	**Demethylated**
C (%)	39.1	42.05	67.27
H (%)	8.7	10.14	11.43
N (%)	0	< 0.05	< 0.05
O (%)	52.2	43.32	17.06
S (%)	0	0.078	< 0.05
H_2O (%)	0	1.03	1.47
Ash (%)	0	3.06	2.23
Ca (ppm)		< 23	119
Na (ppm)		11600	17500
K (ppm)		628	541
Cl (ppm)		124	154
Mg (ppm)		< 8	29
P (ppm)		2220	1750
HHV (MJ/kg)	16.0	21.8	20.6

pressure than would be expected for its molecular weight. Low vapor pressure is a characteristic of alcohols, water and other polar compounds and is the result of molecular association. Glycerin causes less reduction in water's vapor pressure, which can be explained by molecular contraction, an effect that is attributed to hydrate formation [30].

Many researchers report different values for glycerol's LHV. Soares et al. [32] report a LHV (low heating value) of 16.07 MJ/kg, Silva and Müller [33] report 16.18 MJ/kg; Vaz et al. [34] report LHV of approximately 19.0 MJ/kg, while Thamsiriroj and Murphy [35] report LHV 19.2 MJ/kg for glycerol obtained as a byproduct of biodiesel production using seeds and 14.82 MJ/kg for glycerol obtained from fat residue. Combustion heat of first use oils has an average of 19.56 MJ/kg which is around 10% higher than that of pure glycerol, which is 17.96 MJ/kg [36].

Table 3
Analysis results of macro elements carbon and nitrogen measurement in crude glycerol [12].

Feedstock	Ida Gold	Pac Gold	Rapeseed	Canola	Soybean	Crambe
Calcium (ppm)	11.7	23	24	19.7	11.0	163.3
Potassium (ppm)	BDL	BDL	BDL	BDL	BDL	216.7
Magnesium (ppm)	3.9	6.6	4.0	5.4	6.8	126.7
Phosphorus (ppm)	25.3	48.0	65.0	58.7	53.0	136.7
Sulfur (ppm)	21.0	16.0	21.0	14.0	BDL	128.0
Sodium (%wt)	1.17	1.23	1.06	1.07	1.20	1.10
Carbon (%wt)	24.0	24.3	25.3	26.3	26.0	24.0
Nitrogen (%wt)	0.04	0.04	0.05	0.05	0.04	0.06

BDL indicates values that are below the detection limit for corresponding analytical method. The detection limits in ppm were as follows: calcium—2, potassium—40, magnesium—0.20, sodium—80, phosphorus—5, sulfur—15, carbon—200 and nitrogen—100.

Table 4
Average viscosity and heat of combustion of crude glycerol from different feedstock [12].

Feedstock	Ida Gold	Pack Gold	Rapeseed	Canola	Soybean	Crambe
Viscosity at 40 °C (cP)						
Crude glycerol	8.80	8.67	8.50	8.46	8.65	8.50
HHV (MJ/kg)						
Crude glycerol	18.600	19.428	19.721	20.510	19.627	19.472

Glycerol's caloric value depends on the raw material that was used to produce it. It is twice that of fossil fuel but is comparable with the combustion heat of most types of biomass, such as wood, straw, oilseed cake, bark, sawdust, etc [37]. Table 1 lists the most important physical and chemical properties of glycerol.

2.2. *Characterization of crude glycerol*

The term "glycerol" is only applicable to the pure chemical compound 1,2,3 propanotrial, while the term "glycerin" normally applies to purified commercial products with contents of higher than 95% glycerol. They differ slightly in glycerol content and other characteristics such as smell, color, and traces of impurities [41]. Many grades of glycerin are commercially available. They are obtained after removing salts, methanol, and free fatty acids. Methanol is generally recovered by heating and reused in the biodiesel production process. In most commercial applications the quality of glycerin must be improved until it has an acceptable purity that is completely different from those obtained in biodiesel facilities [18,42].

There are many actions and processes used to purify biodiesel, recover useful agents for re-cycling, and process the byproduct glycerol [43]. An important post-process of glycerol includes acidification/neutralization to adjust pH and evaporation/distillation to separate water and excess methanol for reuse. Biodiesel manufacturers normally make an effort to recover excess non-reactive methanol. However, because recovery of methanol is less cost effective than using new methanol, this is not always the case [44].

Methylated glycerol contains 50 to 70% glycerol, 10 to 20% methanol, 5 to 10% salts, < 3 to 10% water, < 1 to 5% fatty acids, and 5% non-glycerol organic material (NGOM) by weight. Demethylated glycerol typically contains 70 to 88% glycerol,

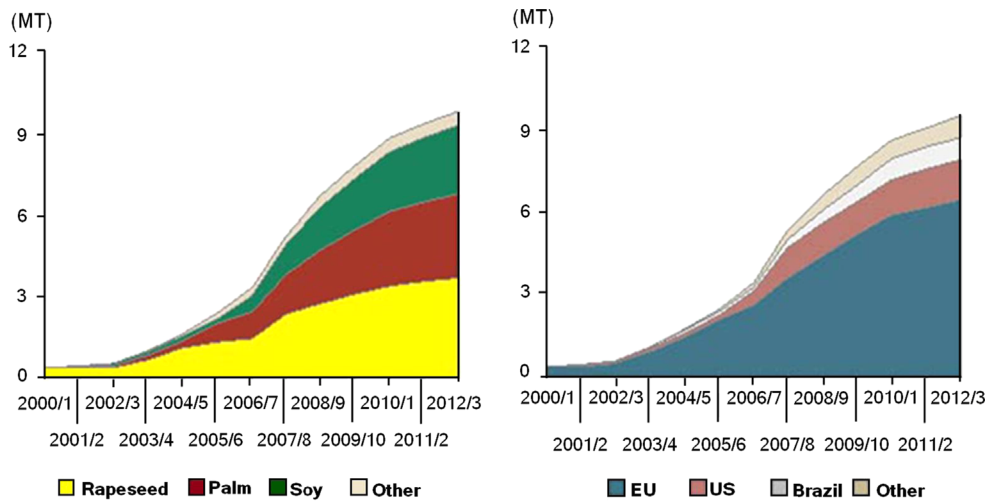


Fig. 2. Worldwide use of vegetable oil for biofuel production [60].

<1% methanol, 5 to 15% salts, <5 to 15% water, <1 to 5% NGOM by weight [45].

Table 2 shows an analysis of three types of glycerol. Values for USP grades are included for comparison. All three types (USP, methylated and demethylated) contain significant levels of oxygen (52, 43, and 17% by weight, respectively). However, the low value measured for demethylated glycerol could indicate a reasonable concentration and larger amounts of NGOM.

Frequently, the triglycerides contained in vegetable oil and or fat are now used as sources of biodiesel, generating raw glycerin (or raw glycerol), which is the most common form that biodiesel producers sell [18]. This low-grade glycerol also contains water, salt, and other organic materials, including residual methanol as well as free fatty acids. Each component varies quite a bit in content depending on the raw material used [12].

Thompson and He [12] characterized glycerol obtained in biodiesel production utilizing various raw materials, finding that the glycerol content is in the area of 60 to 70% by weight. Use of mustard seed as a raw material generates lower glycerol (62%), while using soybean oil as a raw material gives 67.8% glycerol. The methanol content was from 23.4 to 37.5%, which is reflected in its low viscosity. Table 3 shows the analytical results of crude glycerol characterization while Table 4 shows the viscosity and LHV of crude glycerol obtained from different raw materials obtained by Thompson and He.

3. World glycerol production and market

World production of biofuels has been rapidly increasing for the last decade. Biodiesel production in the European Union has grown exponentially [12,14,24]. Among the main reasons for the increase in production and demand of biodiesel is the increase in oil prices. Global climate change and improving energy stability have become a growing concern throughout the world. The benefits for agriculture and rural regions are an opportunity to increase economic development in many developing nations [46,47].

But the viability of the first generation of biofuels has been plagued with concerns about substituting food products, effects on the environment, and climate change because it is mainly produced from the harvest of food such as grain, sugar cane and vegetable oil [9]. The biodiesel economy as well as that of glycerol could be influence by the way in which glycerol and other byproducts are utilized [48].

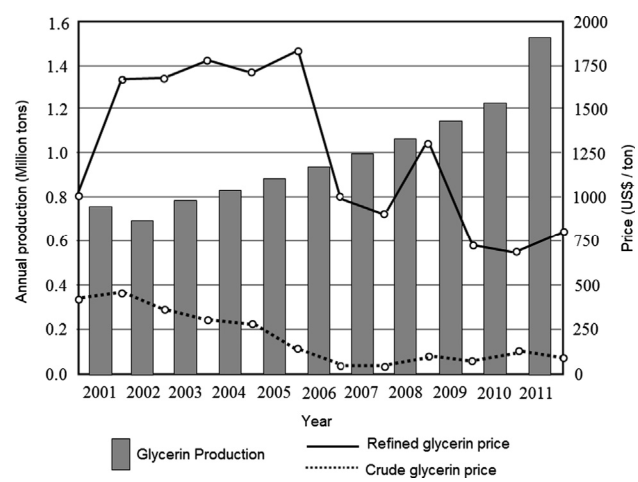


Fig. 3. Projection of global glycerol production and prices.

3.1. World biodiesel and glycerol production

The European Union has been producing biodiesel on an industrial scale since 1992 [49]. After 20 years of commercial use in Europe, biodiesel has proven its value as an alternative fuel in diesel motors [50,51]. Crude glycerol production from these processes has increased at the same rate and if sustainable growth is expected in the future, it is assumed that there will be an excess of glycerol on the world market [52]. In 2003, the European Union was the largest producer of biodiesel; it produced 82% of the biodiesel [53] in the world. According to the European Biodiesel Council, EU production was 5 million metric tons (MMT) in 2006. There had been a dramatic increase of 28% per year since the year 2000. In 2006, world production was 10 million cubic meters of biodiesel [49]. According to Oil World's estimate, production was 16.7 MMT in 2007. This significant growth took place mainly in the European Union and the United States [49]. What's more, European Union Directive 2003/30/CE stated that by the year 2010, member nations were required to use 5.75% biofuel in their petroleum-based fuels used for transportation, calculated based on energy level [54]. Application of this rule would lead to an increase in biodiesel production, which was estimated to reached 10 MMT per year by the year 2010, meaning that 1 MMT of glycerol would be produced per year [14]. However, an estimate for 2008 showed that world biodiesel production reached 10.8

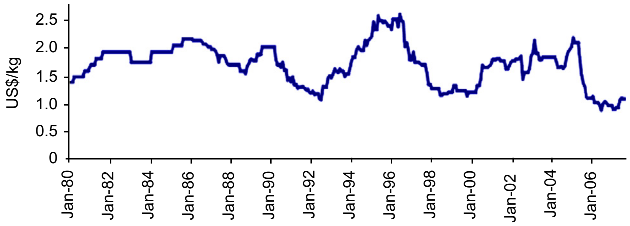


Fig. 4. Historical prices of 99.5% refined glycerin (USP) [69].

MMT; 60% was produced by the European Union, 20% by the United States and the remaining 20% by other producers. This shows that the growth trend for biodiesel production and production deadlines were reached before the time forecast [55].

Finally, in 2008 global production reached 11.1 MMT and global capacity reached 32.6 MMT [55]. The world market for biodiesel is expected to reach 37 billion gallons by 2016, an average growth of 42% per year. This means that around 4 billion gallons of crude glycerol will be produced that year [56]. In 2009, the European Union reported production of 20.9 MMT; two countries, France and Germany, produced more than 7.7 million tons. However, the European Biodiesel Council (EBB) bases its data on capacity declared by the existing production facilities. The real quantity of biodiesel produced is probably less [37].

According to the US Department of Agriculture, global annual production of the main vegetable oils in 2007/08 reached 128.8 MMT, increasing to 133.9 MMT in 2008/09. In 2009/10, 141 MMT were forecast; for 2010/11 it was 148.6 MMT; even reaching 156.8 MMT for 2011/12 and 159.64 MMT in 2012/2013 [57]. What's more, in small production plants, approximately 31 million tons of vegetable oil and animal fat are produced and consumed each year [58]. In 2009, US biodiesel production exceeded 10.2×10^9 L (2.7×10^9 gal), on the other hand, the U.S. biodiesel industry reached a key milestone by producing more than 1 billion gallons of fuel in 2011, according to year-end numbers released by the EPA in January 2012 [59]. Recent decreases in the price of diesel and the slim margin it generates has had negative effects on the biodiesel industry in such that it is estimated to be currently operating at less than 25% of this capacity. However, even with reduced utilization, the glycerol market is nearly saturated [44]. Fig. 2 shows statistics for use of vegetable oil from the main seeds to fabricate biofuel.

In Europe, glycerin comes from transformation activities based on vegetable oil, fat and animal tallow. Crude glycerin in the US mainly comes from biodiesel refineries. In Asia, glycerin is derived from vegetable oil. The largest source in Malaysia and Indonesia is palm oil; in the Philippines it is coconut oil [61]. According to market research, today the Asia-Pacific region is the largest glycerin producer in the world [62]. In 2007, Asia was responsible for more than 44% of world production and Western Europe was the second, producing around 35%. These two regions and the United States were responsible for at least 91% of world production that year [63].

Global consumption of glycerol in 2008 was nearly 750 thousand tons [64]. In 2009, 194,000 t of glycerol were produced in the United States [65]. It's been estimated for 2010 that plans announced for biodiesel production would add 2.2 million tons of glycerol to the current production in the United States and European Union. However, for 2011 it's been forecast that more than 318 thousand tons of glycerin would reach the North American market, a 59% increase over 2009 production [65]. One report forecast that world glycerin production should reach 2 million tons in 2015 [62]. Fig. 3 shows world glycerol production and price statistics for 2010.

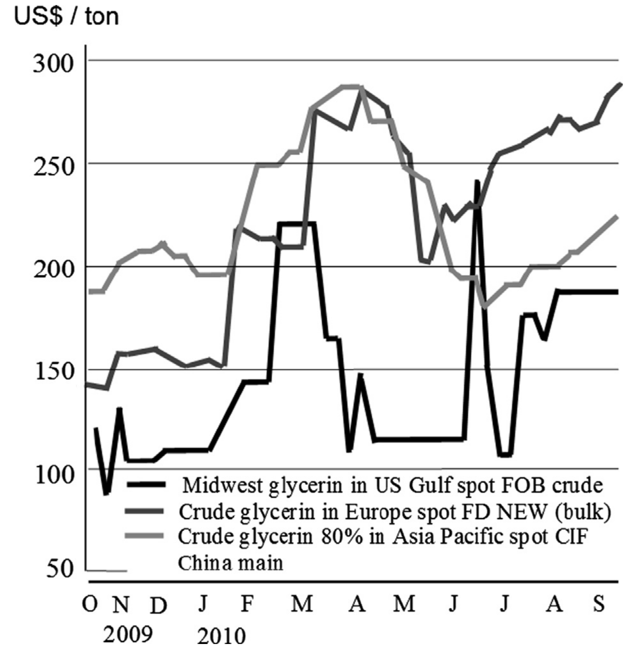


Fig. 5. Volatility of glycerol prices on global markets [67].

3.2. Biodiesel and glycerol consumption market

As biodiesel production has increased, glycerol production has grown and saturated the market [66]. In 2005, world glycerol demand was estimated at 900 thousand tons [13]. For 2007, Asia was the largest consumer of refined glycerin with 25% of consumption. Western Europe was the second largest refined glycerin consumer, with 28% of world consumption in 2007. North America was the third largest consumer. These three regions accounted for 82% of world consumption in 2007 [63].

Generally Europe imports refined and crude glycerin from Asian countries. It is considered a typical importer of this resource. The United States is also a glycerin importer, receiving product from Indonesia, Malaysia, Argentina, and Europe. Asia exports on a large scale to global and regional markets, and glycerin is a local end product. In recent years China has surged in the market as a large importer, in addition to having local production [67]. What's more, due to the growing petroleum and chemical industries in Asia, much of the glycerin production had before been exported to the United States, but with growing freight costs, most of this production ended up going to China [68]. The Asia-Pacific region overtook Europe as the largest market in 2009 and is now the largest regional market with the fastest growth in the world, propelled by the increase in glycerin applications in various sectors such as pharmaceutical, personal hygiene, food and beverage products. There are lower importation rates in some Asian markets. This market had predicted annual growth of about 3.3% per year from 2007 to 2015 [62]. New refined glycerin markets are also largely responsible for projected growth of world demand from 2007 to 2012, and for 2012 Asia is still expected to be the largest market due to increased demand for many applications including new markets for refined glycerin [63].

The worldwide glycerin market is known for its unpredictable and complex nature, since it is a byproduct. Production of the chemical is directly affected by the demand by various end-use segments. Demand for glycerin plummeted from 2008 through 2009 because of a slump in the macro economy. The negative impact of the recession was clearly evident in many regions. Nevertheless, the glycerin market is expected to recover by

2011/2012 and sustain growth in the ensuing years. In addition, usage of glycerin in various new applications is expected to improve glycerin demand in the near term [62]. However, the glycerin market recovered in 2012 and sustains growth for the following years. It is expected that by 2016, China will account for 27% of the world's refined glycerin consumption. [63]. Thailand will also experience high growth rates as a result of epichlorohydrin production. Both Indonesia and Malaysia will continue to export large amounts of refined glycerin. Japan's refined glycerin consumption growth is expected to remain flat in the next several years. Overall, Asian consumption will significantly increase to 45% of the global refined glycerin total in 2016 [63].

3.3. Current world glycerin and glycerol prices

From the 1970s until the year 2004, high-purity glycerin had a stable price between 1200 and 1800 US$/ton. Market and production conditions were stable (Fig. 4). When prices were high, users reformulated their production with alternatives such as sorbitol or synthetic glycerin, while low prices encouraged the use of glycerin in other applications, taking the place of petrochemicals. This relatively stable market has been drastically altered by the arrival of biodiesel. With stable prices, there was no need to obtain historical glycerol prices for the savings of the biofuel industry because in the traditional petrochemical market, the value of glycerol was essential to maintain the business model. Though the petrochemical industry did know that biodiesel would succeed and the volumes would be large, they were incapable of understanding how effective it would be [13].

The subsidy policies and regulations proposed in the United States and the European Union for transportation fuel rose the production of biodiesel and its by product, glycerol. Growing amounts of glycerol began to be dumped onto a relatively stable market and in 2005 the stable prices went into free fall. The volumes of glycerol were enormous and are growing.

Most chemical companies involved in glycerol production had problems purifying it or eliminating it because of its high cost, which lead various businesses to close [39,70–73]. In Europe, where the market is very dynamic, local production and importation lead to an important role in defining prices [67], causing a collapse in the price of crude glycerol. The price has fallen by a factor of 10 in recent years [66]. The large amount of glycerol largely derived from palm oil in countries like Malaysia and Indonesia (the largest glycerol producers) played a part in the price of glycerol falling to 33 cents per kilogram or less [69,74].

In 2003, refined glycerin cost around 1200 US$/ton. In 2006, the price stabilized around 600 US$/ton, with a strong falling trend because of growing biodiesel production (Figs. 4 and 5). In 2006, crude glycerin (80% glycerol) cost 125 euros per ton and was forecast at 150 euros per ton for 2008. The price of crude glycerol also fell in 2006. In the US, crude glycerol was quoted between 0 and 70 US$/ton. Most biodiesel producers assign a value of zero to crude glycerol [13]. Figs. 3 and 4 show the historical evolution of crude glycerol and refined glycerin prices. In 2011, the price of crude glycerol in the US is so low, 2 to 5 cents per pound (4 to 11 cents per kilogram), that many biodiesel producers are storing glycerol to wait for a better market [75].

However, glycerol has shown to be a volatile commodity (Fig. 5), with oscillating prices leading to questions about the stability of future glycerol production [76]. In the United States, the glycerol surplus obtained in biodiesel production forced producers to sell crude glycerol for 44 US$/ton and even less. In 2007, new uses of glycerol had pushed priced to 132–220 US$/ton. Refined glycerin prices followed the trend, with low prices wavering from 440 to 660 US$/ton, depending on quality and purity. While new uses for glycerin were expected to help consume the growing volume of crude glycerin, factors of supply and demand dictate the price. For example, in the United States, the market price for crude glycerin fluctuated from 110 US$/ton in January 2010 to US$ 330 a ton in December 2010 [65].

At the end of 2010, it was speculated that domestic glycerin prices in the United States could reach 220 US$/ton in the following months because of Asian and European producers with lower prices than in the US. In the northeast of Europe, local stock prices of vegetable glycerin were assessed at 462 to 506 US$/ton. In Asia, vegetable glycerin was assessed at 506 to 550 US$/ton CFR (cost and freight) in the northeast of China. Even with transportation prices, foreign material might become more desirable and local glycerin values in the US might grow beyond present values. In the Midwest of the United States, vegetable glycerin was priced at 594 to 682 US$/ton free on board (FOB) [61].

For November 2012, glycerin from vegetable oil was quoted at 925–1080 US$/ton and glycerin from animal fat between 892 and 1069 US$/ton, while pharmaceutical USP grade glycerin was quoted at 1410–1565 US$/ton. For the same year, in Europe the price of vegetable oil glycerin was quoted between 974 and 1050 US$/ton and animal fat glycerin from 860–924 US$/ton. There are differing opinions about the price of crude glycerin (80% glycerol), with the majority of the estimates at a price from 500 to 571 US$/ton. In Northeast Asia, refined glycerin prices held at 825–880 US$/ton FOB, while crude glycerin fell to the range from 380 to 450 US$/ton CIF in 2011 for 355–370 US$/ton CIF in 2012. The price of 80% pure crude glycerin obtained in biodiesel production remained at 44 US$/ton because it had been dumped onto the market by the rapid growth of biodiesel production. Glycerin FOB in Southeast Asia was from 860 to 880 US$/ton in April 2011 for 795–860 in November 2012 [77].

4. The glycerol situation in Brazil

Brazil was one of the first countries to use clean energy (in order to reduce CO_2 emissions). The government decided to substitute alcohol for gasoline in 1973 (Proalcool). In the mid 1980s, approximately 95% of cars produced in Brazil were retrofitted to utilize ethanol as fuel. In 2003, flex-fuel vehicles made up more than 80% of new vehicles sold in Brazil. The use of biofuels will certainly continue to grow [78].

The Brazilian Biodiesel Technology Development Program (PROBIODIESEL) was created to bring about the gradual substitution of diesel from petroleum with biodiesel [79]. In 2004 the Brazilian federal government implemented the Brazilian Biodiesel Production and Use Program to add biodiesel to metropolitan diesel made from petroleum. Beginning in 2008, all diesel sold had to be made up of 3% biodiesel; this percentage rose to 4% in 2009 and 5% in 2010 [80]. B20, a mixture of 20% biodiesel and 80% diesel, is scheduled for introduction in 2020 [81]. Implementation of this program will cause a glycerin glut. It's estimated that with 4% biodiesel, the glycerin surplus is around 264 thousand tons per year, and with the addition of 5%, will reach 325 thousand tons per year [80]. Endless government incentives fuel the production of biodiesel, which is being produced on a grand scale, producing a glycerin surplus that is harming the biodiesel economy [82].

In the midst of this domestic biodiesel production scenario, the forecast for 2009 was that Brazil would produce around 760,000 m^3 of biodiesel. Production of 76,000 t of glycerol was expected, causing doubts that the excess of highly-polluting glycerol produced might be irresponsibly disposed of in the environment [83].

But the forecasts were low, since the glycerol volume produced in 2008 was more than 100,000.00 m^3 as a consequence of the production of 1.2 million cubic meters of biodiesel needed to fulfill

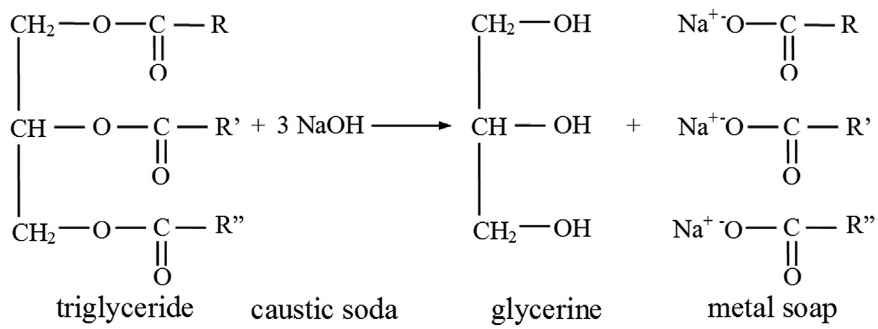


Fig. 6. Basic reaction of the saponification process [98].

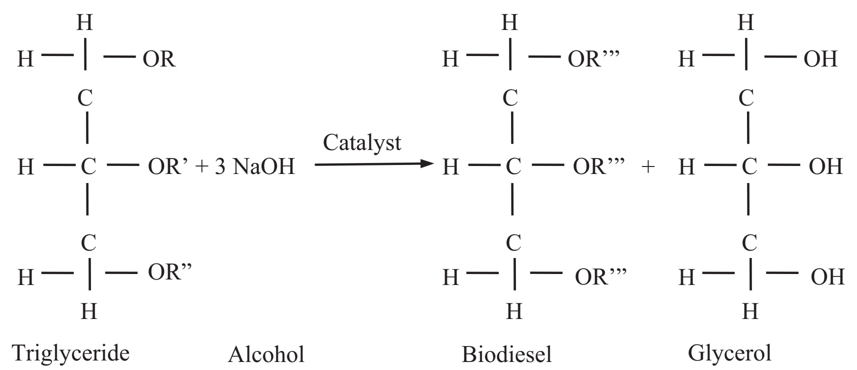


Fig. 7. Stoichiometric reaction of triglycerides and alcohol [102].

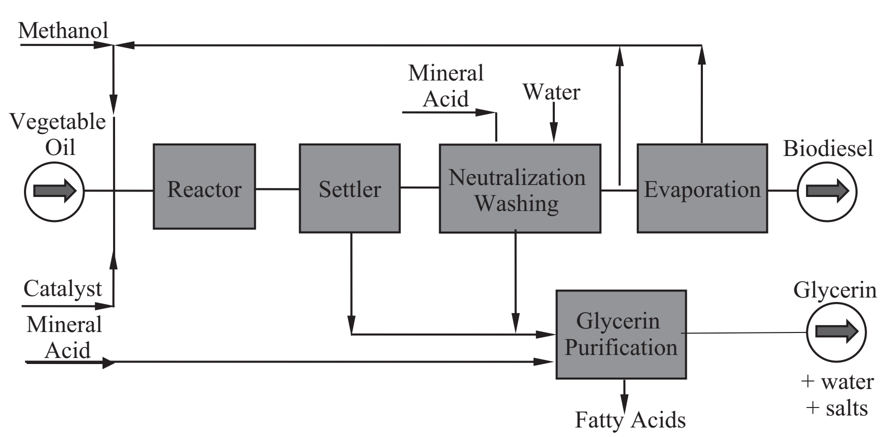


Fig. 8. Global scheme for a typical continuous homogeneous catalyzed process [6].

legislation that established the addition of 2% biofuel to common diesel [84]. In 2010, transesterification of oil and fat in Brazil produced 2.4 million cubic meters, the equivalent of around 240,000.00 m^3 of aqueous glycerin [85]. In 2011, there is a surplus of 100,000 t of crude glycerol. In 2011 had been predicted that in 2013, when the mixture of biodiesel is obligated to rise from 4 to 5%, 250,000 t of crude glycerol will be produced [86]. Today (March 2013), the production of biodiesel is about 2.75 million cubic meters, which suggests that there is a production of approximately 275,000 m^3 of glycerol [85].

According to the Brazilian Industrial Chemistry Association (Abiquim), in 2008 there was a working capacity of the domestic glycerin industry of around 41.5 million liters for a demand that was no more than 30 million liters. For 2009, glycerin production closed at around 160 million liters, and for 2010 production of 230 million liters is forecast [87].

Meanwhile, prices follow the international trend. At the beginning of 2007, the value of crude glycerol (of different grades) obtained from biodiesel production was between 114 and 228 US$/ton [88]. The price of crude glycerin in 2008 was around 62 US$/ton, bi-distilled (96%) was 1235.00 US$/ton, while pharmaceutical USP grade glycerin ($>99.5\%$) was brought to market for 1,470.00 US$/ton [89]. Since crude glycerin production is greater than internal demand is able to process, today crude glycerol is exported to China for prices that vary from 50 to 70 US$/ton. The great challenge facing Brazil will be to incentivize biotechnology research. This has been timidly developed in the country. In addition, the immediate transfer of new technological discoveries the biodiesel mills themselves must be facilitated. This will allow transportation costs for converting to biodiesel to be reduced and will make biodiesel a highly profitable biofuel [88].

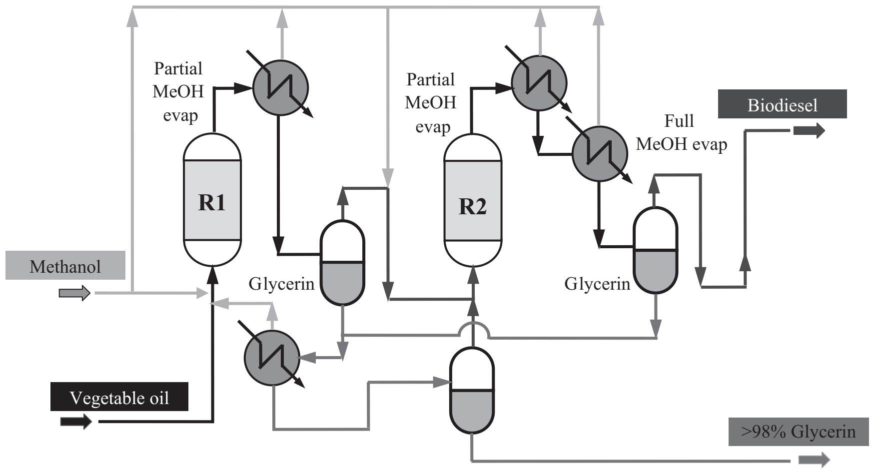


Fig. 9. Simplified flow chart of the heterogeneous process [6].

5. Biodiesel and glycerol production technology

Biodiesel production results in a relatively large amount of byproducts and residue, such as gluten flour, gluten, pulp, waste water and crude glycerol [90]. Glycerol is the main component in all fats and oil and the main by-product with added value produced from oil and fat by means of saponification and transesterification carried out during oil and chemical processes in biodiesel production [37,91,18,92,93–96]. Glycerol is produced in two ways: natural glycerin (as a by-product of soap production or fatty acid methyl esters such as biodiesel) and synthetic glycerol. Natural glycerol is initially produced in a raw form that contains water and other residues as impurities depending on the production process. Generally, glycerin is obtained as a byproduct when biodiesel is produced by transesterification [97]. Crude glycerin is obtained as a result of this process. It is the form of glycerin that is most sold by biodiesel producers [18].

5.1. Hydrolysis

Fat and oil are triglycerides and can undergo basic or alkaline saponification. Acidic saponification simply produces glycerol and the fatty acids that make it up, while basic saponification produces the salts of these fatty acids (Fig. 6). Soap is generally produced as a result of a chemical reaction between a strong base (generally sodium hydroxide or potassium hydroxide) and some fatty acid.

The essence of soap production is the saponification reaction. In saponification, sodium hydroxide or potassium hydroxide react with triglycerides, knocking off glycerol and forming soda or potassium salts which we call soap. Fatty acid is also called soap. Glycerin is extracted from soap with lye—a brine solution that is added to the soap at the saponification stage. Wet soap is soluble in weak brine, but separates out as the electrolyte concentration increases. Glycerine, on the other hand, is highly soluble in brine. Wet soap thus has quite a low electrolyte concentration and is about 30% water (which makes it easily to pump at 70 °C). To remove the glycerin, more electrolyte is added, causing the wet soap to separate into two layers: crude soap and a brine/glycerin mixture known as spent lye, neutral lye or sweet waters [98].

5.2. Transesterification

Biodiesel is typically produced by the transesterification reaction of different triglycerides. When the triglycerides are stimulated by a catalyst, they react chemically with alcohol, generally methanol or ethanol, to produce methyl ester, biodiesel, and ethyl ester, glycerol [11,99–101]. Biodiesel is made using transesterification in three reactions, in which di and mono-glycerides are formed as intermediaries. Traneseterification of triglycerides in Fatty Acid Methil Esters (FAME) is a catalyzed and balanced reaction in which one mol of triglycerides reacts with three mols of methanol (Fig. 7). Though the general stoichiometry of the reaction requires three mols of alcohol for each mol of triglycerides, an excess of alcohol is needed in the reaction medium to force the reaction and obtain a high yield [6,97]. Most industrial processes in biodiesel production use a 6 to 1 M ratio of alcohol to oil, with an excess of 100% of alcohol in order to complete the reaction.

The majority of the excess alcohol (up to 80%) ends up in the glycerol layer after the reaction. Producers recover the alcohol to reuse it [103]. Among the different types of catalysts studied for the transeterification reaction, the most common are alkaline bases. The main examples are alkaline earth metal hydroxides or alkoxides of sodium or potassium. However, transesterification can also be carried out using acidic catalysts such as hydrochloric, sulfuric or sulfonic acid, or using metallic base catalysts such as titanium alcoholates or magnesium, tin, zinc, and aluminum oxide [6,104,105].

Generally in conventional biodiesel industrial processes (Fig. 8), methanolysis of vegetable oil is obtained using a homogeneous catalyst, frequently sodium hydroxide and sodium methoxide [106]. The catalyst is applied either to a load of the raw material or continuously.

Sodium is recovered after the transesterification of sodium glycerate, sodium methylate and sodium soaps in the glycerol phase. The salts must be neutralized with an acid neutralization step, with aqueous hydrochloric or phosphoric acid for example. In this case, glycerol is obtained as an aqueous solution containing sodium chlorate. Depending on the process, final purity of glycerol is around 80 to 95%. When sodium hydroxide is used as a catalyst, there are generally collateral reactions forming sodium soap. This type of reaction is seen when sodium methoxide is employed and there are traces of water. Sodium soap is soluble in the glycerol phase and must be isolated after neutralization by decanting the fatty acid. Loss of esters converted to fatty acids can reach up to 1% in biodiesel production [6,107]. In transesterification, since an excess of methanol is added, two phases are formed: one rich in methanol and one rich in biodiesel. Glycerin is distributed between the two phases, though it is more prevalent in the methanol phase. However, when ethanol is used, separating the phases of the final products is complicated. Methanol is used more often and is totally justified both physically and chemically due to

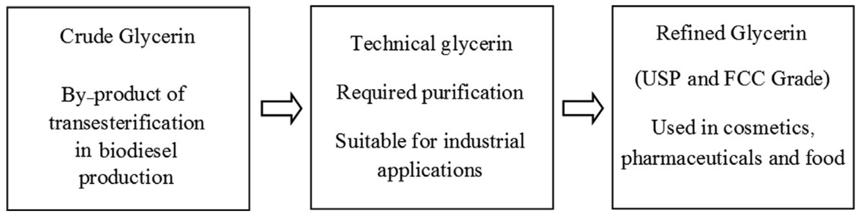


Fig. 10. Types of glycerin and how they are obtained [112].

Table 5
Quality specifications for each grade glycerin [112].

Properties	Crude glycerin	Technical grade glycerin	99.7 USP grade glycerin
Glycerol content	40–88%	98.0% Max.	99.70%
Ash	2.0% Max.	N/A	N/A
Moisture content	N/A	2.0% Max.	0.3% Max.
Chlorides	N/A	10 ppm Max.	10 ppm Max.
Color	N/A	40 Max. (Pt—Co)	10 Max (APHA)
Specific gravity	N/A	1.262 (@ 25 °C)	1.2612 min.
Sulfate	N/A	N/A	20 ppm Max.
Assay	N/A	N/A	99–101% (dry)
Heavy metals	N/A	5 ppm Max.	5 ppm Max.
Chlorinated compounds	N/A	30 ppm Max.	30 ppm Max.
Residue on ignition	N/A	N/A	100 ppm Max.
Fatty acid & ester	N/A	1.00 Max.	1.0 Max.
Water	12.0% Max.	5.0% Max.	0.5% Max
pH (10% solution)	4.0–9.0	4.0–9.1	NA
DEG and related compounds	N/A	N/A	Pass
Organic volatile impurities	N/A	N/A	Pass
Organic residue	2.0% Max	2.0% Max	N/A

ppm—parts per million, N/A—Not applicable.

the short polar chain. Recently, ethanol has become more common because it is less aggressive than methanol and since it is renewable. This process is still in the research, development and optimization phase [108].

The increase in biodiesel production began a search for solid acids or basic catalysts that could be used in biodiesel production [6,107,109]. Some solid metal oxides, such as tin, zinc and magnesium, are known catalysts. They react according to a homogenous mechanism and end up as metal soap or metallic glycolates. In this continuous process, the transesterification reaction uses a completely heterogeneous catalyst made up of a mixture of zinc and aluminum oxide which develops the reaction without losing catalyst. The reaction is carried out at a lower temperature and pressure that those with a homogeneous catalysis, though with excess methanol. This excess is removed by vaporization and recycled for the process. Chemical conversion is reached with two successive stages of reaction and glycerol separation in place of the balanced reaction (Fig. 9).

The catalysis section included two fixed bed reactors fed with vegetable oil and methanol in the given proportions. The excess of methanol is removed after each reaction by partial evaporation. Next the esters and glycerol are separated in a decanter. Glycerol outlets are united and residual methanol is removed by evaporation. In order to obtain biodiesel in the specifications desired, the last traces of methanol and glycerol have to be removed. The methyl ester purification section of the outlet from decanter 2 consists of a final vaporization of methanol in a vacuum followed by final purification in an absorber to remove soluble glycerol [6,107].

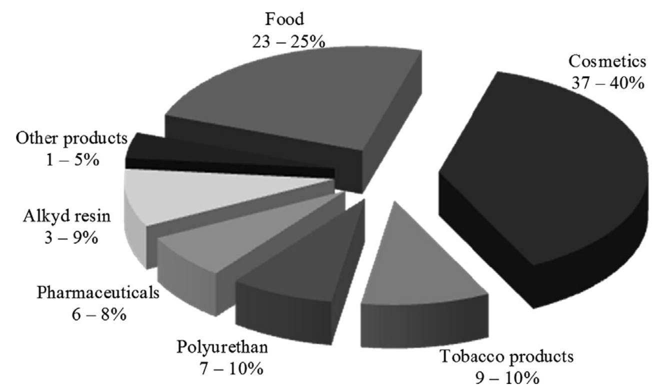


Fig. 11. Traditional glycerol uses with average worldwide values [37].

5.3. Refining crude glycerol

Independent of whether animal or vegetable fat, a mixture of animal and vegetable fat, or synthetic fat are used as the source, in most applications crude glycerol is refined before its final utilization to obtain a higher degree of purity [18,63]. Average composition of crude glycerol generally oscillates between 40 and 70% glycerin, 10% water (in the range of 8–50%), 4% salt (from 0 to 10%), less than 0.5% methanol and approximately 0.5% free fatty acids [37,69]. Despite the many applications for crude glycerol in pharmaceutical, food, industrial, and cosmetic products, refining crude glycerol to a high degree is very expensive, especially for small- and medium-sized biodiesel producers [12,18,110,111]. Crude glycerol is generally treated and refined by filtration, chemical additives, and fractioned distillation in vacuum to produce various types of glycerin. It can also be refined by a method using lower-energy intensive filtration by a series of ion exchanges in resin [102]. The approximate cost of crude glycerol is 0.33 US $/kg [75] and 0.58 US$/kg to obtain more pure glycerin.

There are three basic types of refined glycerin, based on their purity and potential end use. They are: (a) "technical grade", used as a building block in chemical products, not used for the creation of food and medicine; (b) United States Pharmacopeia (USP), glycerin from animal fat or sources of vegetable oil, appropriate for food and pharmaceutical products; and (c) Food Chemicals Codex (FCC), glycerin from vegetable oil sources, appropriate for use in food (Fig. 10). Glycerin is normally sold 99.5% to 99.7% pure. The majority sold today is made to meet the rigorous requirements of United States Pharmacopeia and Food Chemicals Codex. Conventional uses and present market capacity cannot absorb the surplus of crude glycerin. Additional more-expensive purification is needed to obtain industrial grade (tech glycerin) that is 98% pure, which is also available on the market [113]. Quality specifications of various types of glycerin are shown on Table 5.

Later refining of crude glycerol will depend on the economy of scale of production and/or the availability of a purification installation. Large biodiesel producers refine their raw glycerol and distributed it in the markets of the food, pharmaceutical, and cosmetic industries [114].

6. Alternatives for the use of glycerol—New trends

The properties of glycerin have created a versatile range of products. Up to the year 2000, there were more than fifteen hundred end uses in the chemical industry [115]. At present, it is estimated that there are more than two thousand uses for glycerol. However, in the majority of products it is only used in small quantities. There are few end uses that need large amounts of glycerol in their formula. Uses vary from energy bars to cough syrups to sealants for ships. The three main uses for refined glycerin are food products, personal hygiene products and oral hygiene products, making up about 64% of total consumption (Fig. 11). For a long time consumption of oil and fat was divided among food, animal feed, and industrial use at a 80:6:14 ration, but with the increase in biodiesel production this is probably closer to 74:6:20 now and is expected to reach 68:6:26 in 2020 [116], showing that industrial usage has been growing in recent years.

Crude glycerol has a low value because of the impurities. End use of glycerol varies depending on the raw material and the biodiesel production process [12]. If crude glycerol is utilized to produce glycerol derivatives, it will be more valuable [117] and help to improve economic viability of the biodiesel industry, and at present alternatives uses of crude glycerol are being sought.

Due to the large surplus of glycerol formed as a by-product during the production of biodiesel, new opportunities for converting glycerol into value-added chemicals have emerged in recent years, which will definitely promote the commercial viability of biodiesel and further development. Glycerol can be converted into promising commodity chemicals and fuels through chemically selective catalysis, such as selective oxidation, selective hydrogenolysis, catalytic dehydration, pyrolysis and gasification, selective glycerol transesterification and esterification, selective etherification and carboxylation and other processes [56]. Thus there has been an ample field of research in order to find new applications for this raw material at the low cost expected [15,118].

Selective oxidation processes include: (1) oxidation of primary hydroxyl groups, which yields glyceric acid and also tartronic acid; (2) oxidation of the secondary hydroxyl group, which yields the important fine chemical dihydroxyacetone (DHA) or ketomalonic acid; and (3) oxidation of all three hydroxyl groups, which yields the highly functionalized molecule mesoxalic acid [56]. Extensive research concerning selective catalysis of glycerol to produce glyceric acid [119–125], DHA [126–130], and mesoxalic acid was conducted. All the functional derivatives obtained have commercial value. For instance, DHA is the main active ingredient in all sunless tanning skincare preparations and might be a building block of new degradable polymers if the market price is lower [131,132]. Mesoxalic acid is a potentially valuable chelating agent that can be used as intermediate compounds for the synthesis of fine chemicals and novel polymers [56].

Catalytic conversion gives propylene glycol, propionic acid, acrylic acid, propanol, propanediol, [133–136] citric acid, sophorolipids, and other products [15,137]. Selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen can produce 1.2-propanediol (1.2-PD), 1.3-propanediol (1.3-PD), or ethylene glycol (EG). 1.2-PD is used for polyester resin, liquid detergent, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, hygiene products, paint, animal feed, antifreeze, etc. 1.3-PD is used in specialty polyester fibers, films, and coatings. EG is a raw material for synthetic fibers and explosives [138].

Catalytic dehydration of glycerol can produce acrolein, which is a versatile intermediate largely employed by the chemical industry for the production of acrylic acid esters, super absorbent polymers, and detergents [56,139].

Pyrolysis and gasification of glycerol were also found by many researchers to generate CO, H_2. Glycerol is a readily digestible substance that can be easily stored for a long time. The relatively high energy content in the crude glycerol phase also makes it an interesting substrate for catalytic reforming resulting in hydrogen and carbon monoxide, called syngas, by steam reforming in smaller reactor volumes [32,140–143] and production of H_2 by reforming glycerol [142]. Is used in production of fuel oxygenate Acetal (2.2-dimethyl-1.3-dioxolan-4-yl) [144].

Selective glycerol transesterification and esterification can yield monoglycerides (MG) and polyglycerol esters (PEG). MG can be applied as emulsifiers in the food, pharmaceutical, and cosmetic industries [145]. Melero et al. [14] reported the esterification of glycerol with acetic acid to produce glycerine acetates, such as diacetylglycerol (DAG) and triacetylglycerol (TAG), which have been shown to be valuable petrol fuel additives leading to either enhanced cold and viscosity properties when blended with diesel fuel or antiknocking properties when added to gasoline. A glycerol-based fuel additive, glycerol tertiary butyl ether is an excellent additive and there is a lot of potential for diesel to be synthesized via etherification of glycerol [146–148].

Selective etherification of glycerol can yield more valuable fuel additives or solvents with suitable properties. Among these, *tert*-butyl ethers exhibit potential for use as diesel fuel additives in gasoline. They offer an alternative to oxygenates such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE). Selective etherification can also convert glycerol into polyglycerol (PG) and PEG, which have been recommended to be used as biodegradable surfactants, lubricants, cosmetics, food additives [149–151].

Carboxylation of glycerol can produce glycerol carbonate. A lot of attentions have been given to this new and interesting material in the chemical industry [152–154]. Inexpensive glycerol carbonate can be utilized as source of new polymeric materials.

New applications have been found in the polyglycerol, polycarbonate and polyurethane industry in the field of stabilizing wood and production of small molecules such as glyceric acid, hydroxipyruvic acid and glycerol carbonate [155,156]. Recently, the production of 1.3-propanodiol (1.3-PD) or trimethylene glycol (TMG) is gaining increasing importance due to its role as a monomer in polyester synthesis processes for tissues and textile applications, which require a large increase in the production of this product [157].

Glycerol can also be used to prepare dichloropropanol (DCP) [158] and as substrate to produce organic solvent tolerant lipase [159]. Polypropylene can be made from glycerin. This plastic is used in vehicles, appliances, disposable syringes, cleaning products, etc [160].

In biological conversion, many known microorganisms can naturally utilize glycerol as their only source of energy and carbon [92,161–163] utilized in biological methane production from crude glycerol by anaerobic digestion [28,109]. The higher level of sugar reduction allows reduced chemical products to be obtained, such as succinate, ethanol, xylitol, propionate, and hydrogen at higher yields than those obtained using sugar [39].

As it has been mentioned, glycerol can also be used in conversion to chemical commodities (such as propylene glycol, propionic acid and isopropanol). It is also used in fertilizers [29] and as a carbon source for bioreactors treating Acid Mine Drainage [164]. In Agricultural usage, there are other advantages that include low need for nutrients, energy savings and generation by stabilized digestors that improve soil quality [143].

Glycerol from biodiesel might be used as an energetic supplement for cattle [29]. It also has the potential use as an ingredient in various stages of production of Broiler feed [165] and pig feed [165–170]. Roger et al. [166] report successfully including glycerin from biodiesel at low concentration in animal feed.

Table 6
List of various applications of glycerol.

Products	Process	Uses	Major research
Hydrogen	Steam reforming, partial oxidation, auto thermal reforming, aqueous-phase reforming and supercritical water, photofermentation using a photosynthetic bacterium	New fuel and energy carrier that could be used in the transport sector, power generation, chemical industry, photovoltaic cells	Adhikari et al. [142], Slinn et al. [172], Byrd et al. [173], Sabouring and Hallenbeck [66], Ito et al. [174], Huber et al. [175], Wen et al. [176], Zhang et al. [177], Caetano and Silveira [178], Pagliaro and Rossi [179], Wena et al. [180], Menezes et al. [181], Cortright et al. [182]; Tuza et al. [183]; Wang et al. [184]; Kamonsuangkasem et al. [185]; Gutiérrez et al. [186]; Reungsang et al. [187]; Lin [188]
Fuel additive	[a]Reactive of glycerol with acetic through acetylation or esterification process. Reaction of glycerol with ether substrate through etherification process. Reaction of glycerol with acetone and acid anhydride through acetalation process. Glycerol fermentation by *Clostridium pateuriunum*	These products may have suitable properties for use as solvents or additives in gasoline/petroleum engines without changes in design. Uses as brake fluids, as perfume based, as paint thinner and hydraulic fluid	Beatrice at al. [171]; Karinen and Krause [189], Noudreddini et al. [190], Kiatkittipong et al. [191], Fernando et al. [192], Rahmat et al. [24], Garcia et al. [144], Melero et al. [14], Melero et al. [193], Klepakova et al. [194], Ferreira et al. [195], Agnieszka et al. [196], Clacens et al. [149], Klepakova et al. [197], Richter et al. [198], Tran et al. [199], Alhanash et al. [200], Chiu et al. [201]
Methanol	Via synthesis gas	Chemical feedstock, medical and industrial application	Gutiérrez et al. [202]; Goetsch et al. [203], Tsang et al. [204], Duan et al. [205]
Ethanol	Bioconversion of raw glycerol (glycerol fermentation by *E. coli*.	Used as fuel in the space, industrial and transportation sector. Largely use in alcoholic beverages, medical applications and chemical feedstock	Yazdani and Gonçalves [17], Ito et al. [174], Posada and Cardona [206], Oh et al. [207], Amaral et al. [208],
Animal feed	–	Cow and other animal feed, pigs diet, poultry feed. Animal nutrition industry	Dedrain et al. [209], Cerrate et al. [165], Donkin and Doane [168], Donkin et al. [210], Carvalho et al. [211], Oliveira et al. [212], Schieck et al. [213], Li et al. [214], Roger et al. [166], Chung et al. [215], Kansedo et al. [216], Ferraro et al. [217], Wang et al. [218], Fisher et al. [219], Casa et al. [220]
Food	–	Preservation, sweeteners and thickening agent	Irieb [221], Lee et al. [222]
Acrolein	[a]Glycerol conversion: – on hot compressed water – by micro- and mesopourus ZSM-5 – Over activated carbon-supported – Over silica-supported heteropolyacid Reaction gas phase glycerol/water mxture by zeolite Silicotungstic acids	Detergent, super absorber, acrylic acid, polymers	Rahmat et al. [24], Watanabe et al. [223], Corma et al. [224], Zhou et al. [225], Tsukuda et al. [226], Ning et al. [227]
Chemical industry products	[b]Glycerol fermentation by *klepsiella Pneumoniae*. [c]Glycerol selective dehydroxylation. [b]Glycerol hydrogenolysis. [d]Glycerol with CO_2 (glycerol carbonate), Glycerol with heteropolyacid (DCP), glycerol with hidrocloric acid catalyzed by acetic acid as acid catalyst	– Polymer industry (use as monomer in the synthesis of several polyester and polymers, unsaturated polyester) – Plastic industry (polyglycerol methacrylates) – Textile industry (as a substitute for petroleum-based polypropelene, sizing and softening to yarn and fabric) – Explosives industry (nitroglycerin),—Antifreeze liquid – - Additive for liquid detergent	Rahmat et al. [24], Cardona et al. [228], Wang et al. [229], Gong et al. [230], Rosa et al. [231], Villamagna and Hall [232], Pagliario [15], Aresta et al. [154], Lee et al. [158], Lee et al. [233]
Pharmaceutical products	Glycerol oxidation for produce Dihydroxyacetone and crude glycerol with microalgal culture (DHA)	Used as a tanning agent in cosmetics industries, additive in drugs, love potion, health supplements and nutrient	Stella [234], Bauer et al. [235], Pollington et al. [236], Demirel et al. [237], Ciriminna et al. [129], Chi et al. [238]
Biogas	Co-digested in anaerobic digesters, syngas production	Fuel	Skoulou et al. [239]; Robra et al. [240], Amon et al. [241], Siles et al. [242], Fountoulakis and Manios [243]

[a] Adapted by Rahmat et al. [24].
[b] Cardona et al. [228].
[c] Wang et al. [229].
[d] Aresta et al. [154].

Another possible use is as boiler fuel to reduce the thermal energy in the transesterification and/or cogeneration to produce electricity. Directly burning glycerol could be a possible use for large quantities without needed to refine it. This point will be dealt with below.

To sum up, glycerol can be converted into many value-added products through catalytic processes. However, there are additional challenges since the glycerol obtained as a by-product from the biodiesel industry is crude and impure. Zhou et al. [136] stated the following four challenges that must be faced in their review article: (1) New application and products for directly using crude glycerol need to be found; (2) A cost effective purification process needs to be developed to purify crude glycerol from biodiesel processes; (3) There separation of crude glycerol must

be combined with catalytic conversion; and (4) direct bio-catalytic conversion using crude glycerol should be investigated and developed to make it economically practical.

Etherification of glycerol with *tert*-butyl alcohol and isobutylene allowed to Beatrice et al. [171] to identify the suitable experimental conditions required to obtain a mixture predominantly composed of higher glycerol ethers. These researchers studied the processes for converting glycerol in an oxygenated fuel additive (glycerol alkyl–ether) suitable for blending with diesel and biodiesel.

Next, Table 6 presents a summary of the main applications of glycerin, its processes, uses and major investigations (other more than those already mentioned) conducted with each application.

6.1. Glycerol combustion

The main energy generation and atmospheric pollution emissions problems facing the world come from burning fossil fuel in combustion chambers. Industrial combustion is defined as a chemical reaction in which an oxidant (oxygen, generally taken from atmospheric air) reacts with a specific reducer (fuel) in an exothermic reaction (producing energy). Standard dry air is made up of approximately 23.15% oxygen and 76.85% inert gas, nitrogen among them [244]. Other combustion products can also be formed, such as NO_x from oxidation of nitrogen. Most conventional fuel also contains small quantities of sulfur (S) which is oxidized during combustion forming sulfur dioxide (SO_2) or sulfur trioxide (SO_3). Fuels can even contain substances that are not oxidants, such as mineral material (ash), water, and inert gas.

Glycerol is biologically produced, renewable, and biodegradable. Its production process is associated with the green refining industry, which is a great environmental value, as well as encouraging independence from fossil fuel [24]. Its use, including burning it as fuel, does not increase atmospheric pollution globally. The use of glycerol as a fuel in industrial processes has several advantages. Burning industrial glycerol has shown itself to be the simplest method of using crude glycerol. It is also advantageous since it does not require any purification. If combined with biodiesel production, this alternate energy would have additional advantages in energy integration, eliminating the cost of transportation and use of fossil fuels [245].

Though it is known that glycerin has a moderate calorific level (~16 MJ/kg), it has not yet been used as a fuel [24,44,78,171,246–249]. The stoichiometry for burning glycerol is [37]:

$$C_3H_5(OH)_3 + 3.5O_2 \rightarrow 3CO_2 + 4H_2O - 1655\ \text{kJ/mol}$$

However, crude glycerin production process is not easy from the technological point of view. Some of the difficulties of burning glycerol cited by researchers [44,245] are: (a) it has a low calorific value, which makes it incapable of maintaining a stable flame in a conventional burner, as well as being harmed by the water in the mixture; (b) it has a high self-ignition temperature, approximately 370 °C in comparison to gasoline, 280 °C, and kerosene, 210 °C; (c) burning glycerol can form acrolein; (d) it is highly viscous at room temperature (kinematic viscosity approximately 450 cSt), making it hard to atomize with conventional atomizers; (e) its salt content causes corrosion problems in burner injectors and in post-combustion systems, and is also a flame inhibitor, which makes it difficult to burn glycerin.

Glycerol's calorific value depends on the raw material used to produce it, varying from 18.6 to 20.5 MJ/kg using different oily seeds [12]. The heat of combustion is half those of fossil fuels, but is comparable with other types of biomass, such as wood, straw, oilseed cake, cane cake, bark, and sawdust. Its calorific value is low because of the relatively large amount of water that it is obtained with. Glycerol has not yet been co-burned on a large scale with other liquid or solid fuel [37]. Based on its ignition point, direct thermal use of crude glycerol is an obvious choice. Studies have reported that co-burning of crude glycerin with other biomass had favorable results [12]. An attractive and relatively simple option for glycerol it to use it as furnace fuel to produce heat and electricity [250]. According to DAF [251] and Bombos et al. [252], modern boilers are designed to withstand high thermal loads in the furnaces, so using glycerol directly in existing boilers is unacceptable because of the high ignition point and low adiabatic flame temperature. Today, the most common use of crude glycerin is incineration [251]. Thus, assuming that crude glycerin has an average calorific value of 18.5 MJ/kg and an average cost of 10 cents per kilogram, the thermal energy produced would have an average cost of 0.0054 US$/MJ, which is a little less than the equivalent value in natural gas today. However, this is considered the least valuable way to use glycerin since it does not add value to biodiesel production and is sold at the price of an industrial by-product. The cost of biodiesel has two aspects: the raw material feedstock cost and production cost. The recovery of the by-product glycerol makes a significant contribution to the latter.

Glycerol has a high self-ignition temperature, which means that more activation energy is needed for the oxidation reaction. Generally standard combustion burns with a single spark generating a self-sustaining flame, but glycerol won't self-ignite in these conditions. Even if there is an open flame near a spray of glycerol, the droplets that pass through the flame, burn but do not

Table 7
Fuel characteristics [253].

Properties	Unit	100% Glycerin	10% Glycerin/90% Y.G
Saybolt Viscosity (37.8 °C)	mm^2/s (cP)	44.38 (55.59)	52.48 (48.8)
Specific Gravity (15.6 °C)		1.252	0.929
Flash Point	°C	> 120	199
Ash	% Mass	3.805	0.43
Carbon	% Mass	32.8	70.33
Hydrogen	% Mass	8.56	11.32
Nitrogen	% Mass	< 0.2	< 0.2
Oxygen (by difference)	% Mass	54.55	17.70
Total Sulfur	% Mass	0.085	0.01
Total Chlorine	μg/g	18,150.00	2410.00
Mercury	μg/g	< 0.1	< 0.02
% Water (Karl Fisher)	% mass	12.55	1.46
Calorific Value	MJ/kg	14.61	37.96

Table 8
Summary of emissions tests results [253].

Pollutant	Unit	Results
PM10/PM	$g/N/m^3$	4.58
	kg/h	2.27
Nitrogen oxides	ppm	108.95
	kg/h	1.62
Carbon monoxide	ppm	2.0
	kg/h	0.02
Sulfur dioxide	ppm	20.39
	kg/h	0.42
VOCs	ppm	11.86
	kg/h	0.05
Sulfuric acid mist	ppm	0.10
	kg/h	0.003
Calcium	kg/h	0.06
Potassium	kg/h	0.012
Magnesium	kg/h	0.008
Phosphorus	kg/h	0.045
Hydrogen chloride	kg/h	0.015
Chlorine	kg/h	0.002
Acrolein	kg/h	< 0.0036
Acetaldehyde	kg/h	< 0.0036

Table 9
Summary of emissions tests results [255].

Pollutant	Unit	Results	Process parameters	
Combustion of demethylated glycerin (80% glycerol)			Glycerin consumption	13 kg/h
Particulate matter	g/m^3	11.9	Load	45 kW
Nitrogen oxides	ppm	88	O_2	2.4% v/v
Carbon monoxide	ppm	73	Coefficient of excess air	1.13
Sulfur dioxide	ppm	10	Pressure before atomizer	28 bar
Combustion of stable glycerol emulsion			Emulsion consumed	6 kg/h
Particulate matter	g/m^3	0.5	Load	37 kW
Nitrogen oxides	ppm	277	O_2	3.6% v/v
Carbon monoxide	ppm	100	Coefficient of excess air	1.18
Sulfur dioxide	ppm	993	Pressure before atomizer	10 bar

Table 10
Emissions measured from 7 kW prototype burner and 82 kW refractory-lined furnace [44].

	7 kW prototype burner							**82 kW furnace**	
	USP Glycerol (1.68 kg/h)			Propane (0.576 kg/h)		Diesel (0.618 kg/h)		Methylated	Demethylated
Load (kW)	7.3	7.3	7.3	7.4	7.4	7.3	7.3	80.5	53.9
Φ [a]	0.444	0.392	0.37	0.562	0.488	0.645	0.488	0.63	0.77
SR[a]	2.25	2.55	2.71	1.78	2.05	1.55	2.05	1.58	1.3
NO_x (ppm)	3	3.5	3.6	60.2	62.8	74.7	62.5	146.5	118.3
NO_x at 0% O_2 (ppm)	6.9	9.1	9.6	110.5	135.4	117.8	128.6	235.2	155.5
O_2 (% v/v)	11.8	12.9	13.3	9.6	11.3	7.7	10.8	7.9	5.1
CO_2 (% v/v)	7.3	6.7	6.3	6.8	5.9	7	6.2	12.5	15.4
CO (% v/v)	0	0.01	0	0.01	0	0	0	–	–
THC (ppm)	–	–	–	–	–	–	–	4.7	7.1
Exit temp (°C)[b]	958	901	877	1001	974	986	946	1041	1075
Flame temp. (°C)[c]	1201	1103	1060	1359	1213	1628	1343	1782	1716

[a] Equivalence and stoichiometric ratios determined by excess O_2 in the exhaust.
[b] Temperature measured at the throat of the exhaust for the 7 kW prototype burner and the exhaust of the 82 kW refractory-lined furnace.
[c] Adiabatic flame temperature calculated at stoichiometric ratios listed above.

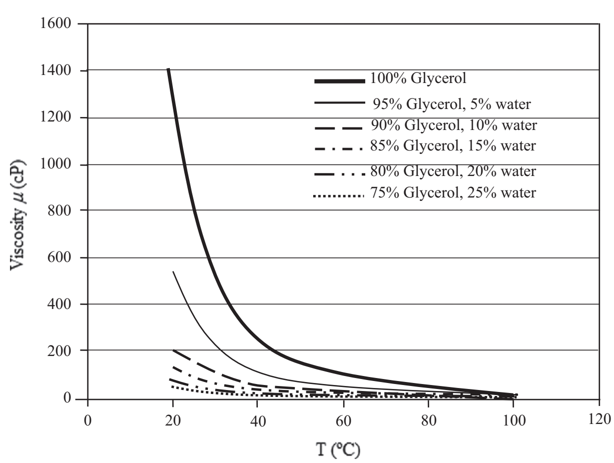


Fig. 12. Viscosity of glycerol and aqueous solutions of glycerol as a function of temperature.

emit enough energy to maintain a continuous combustion reaction [245]. In addition, if there is water present it makes the combustion of crude glycerol very difficult, since it shuts off the flame in the burner and generates a large amount of black carbon. In practice, special burners must be designed to carry out the co-combustion of glycerol with other liquid fuel [37,91,44,245]. Co-burning with other fuels that is easier to ignite would help the ignition process and sustain the flame [256].

It's been reported that burning crude glycerol derived from soybean oil with yellow grease made up mostly of used cooking oil because of the size of a 1970 Kewanee 750 HP industrial fire-tube boiler [253]. Waste glycerin was mixed with waste biomass to produce combustible pellets as an alternative to coal for energy production [254]. Patzer [253] reported that crude glycerin used in small amounts as a mixture, taking into consideration the price on the international market, that it could be a viable fuel, but not when analyzed only as a fuel. He reported that glycerin could maintain a stable flame and had a lot of mineral salt emissions that corrode equipment and reduce its life span. Table 7 shows the basic physical and chemical characteristics of the fuel used by Patzer [253]. Finally Table 8 shows the summary of the combustion results. They are the average of three samples taken at different times during the test.

Stiurgas [255] studied the possibility of using commercial glycerin (80% glycerol) along with stable emulsions of glycerol and heavy oil. According to this author, the final stable emulsion was made up of 1.3% sodium oleate or soap, 3% monoglyceride fatty acid, 8% methanol, 26.5% methyl ester (biodiesel), 27.2% glycerol, and 34% heavy fuel oil. The combustion system used was modified: the adiabatic combustion chamber was pre-heated to 1000.00 °C using natural gas, a modifier burner, 40 bar fuel pump, the fuel was electrically heated to between 60 and 85 °C, and a cyclone to collect and analyze particulate matter. Table 9 shows a summary of combustion results obtained by Stiurgas [255].

Metzger [245] also utilized modified equipment for direct glycerin burning using a 7 kW vortex-type burner and an adiabatic combustion chamber to improve burn and flame stability. This author used laboratory grade glycerol (USP glycerol), methylated glycerol, and demethylated glycerol as fuel.

Bohon [44] continued Metzger's work and improved the burner he'd used before. Through elaborate computer simulations called Computational Field Dynamics, CFD, Bohon [44] improved insulation, operation and experimental usefulness of the burner by diminishing loss and improving stability of the glycerin flame. He also used Metzger's 7 kW burner [245] and an 82 kW vortex type burner linked to a small refractory furnace. The tests were carried out using glycerol USP, methylated glycerol, and demathylated

glycerol as fuel. Table 10 shows the results obtained by Bohon et al. [44].

Acrolein is a product of thermal decompositions of glycerol when it is heated between 280 and 300 °C, which is well below glycerol's self-ignition temperature [251]. Acrolein is toxic in very small quantities, around 2 ppm and some studies suggest human health risk with concentrations as low as 0.09 ppm. Acrolein is increasingly unstable at high temperatures and highly flammable, totally consumed between 930 and 1000.00 °C [256]. It's conceivable that an efficient glycerol flame could consume any acrolein produced before combustion gases are used up in the environment [245,257–259].

Pure or refined glycerol is highly viscous, which makes the atomization process difficult at room temperature [245]. Glycerol's viscosity could be drastically reduced by directly heating it or heating it with steam [258] (Fig. 12), which are the most common methods used in the combustion process. The viscosity of untreated crude glycerol obtained from biodiesel production using oilseed varies from 8.46 to 8.80 cS [12]. Crude glycerol can contain alcohol and water and have a lower viscosity, but producers prefer to evaporate it to recover the alcohol for reutilization. When glycerol is mixed with water, its viscosity is much lower [27] and depending on the quantity of water (for example, 20% by weight) reduction of viscosity can be dramatic (Fig. 12).

The remaining menthol, and sodium and potassium salt and other impurities, must be analyzed because they are known to inhibit various processes [130,260]. Compared to liquid fossil fuel, technical glycerol (minimum 98% glycerol) has a higher mineral content [113]. Mineral compounds sometimes found in glycerol are sodium or potassium chlorates, potassium sulfate, or potassium phosphate. Compounds based on alkaline metals Na and K has high fusion and softening temperatures. As a result, the conditions in which glycerol burns have a great potential of generating slag and pollution increases in comparison with that of liquid fossil fuels [251]. The salt that enters the boilers can become encrusted on the walls and shorten the equipment's life span [261]. If the salt is not removed, it creates significant amounts of ash [91]. Amberlite 252 macroporous resin could be a good choice to remove sodium ions from glycerol/water solutions with high salt concentration [262,263].

7. Conclusion

The problems of diminishing petroleum reserves and the increasing awareness of environmental pollution from petroleum fuel emissions have led to the urge to find renewable alternative fuels as a substitute for petroleum based fuels. The production of ecological fuel components (bioesters, bioethanol) that are manufactured from renewable sources has, in recent days, increased drastically due to the environmental policy in many developed nations of the world. Biodiesel, which has environmental benefits and is produced from renewable resources, has become more attractive. Crude glycerol is produced in significant quantities during the transesterification of triglycerides to produce biodiesel (about 10% w/w) and through the process of saponification.

The global market has been dramatically altered by the arrival of biodiesel. Increasing quantities of glycerol began to be dumped to global market, and prices began to fall, reaching the lowest historical values. When refined to a chemically pure substance, glycerol can be a very valuable by-product of the biodiesel production process, with hundreds of uses. Purification to that stage, however, is costly and generally out of the range of economic viability for small and medium biodiesel industry.

Alternative uses for crude glycerol should be explored to produce a biodiesel increasingly competitive global market. New uses are needed to add value to this residue to optimize process efficiency and reduce the impacts of disposal. Crude glycerol has been widely recognized as an attractive sustainable resource for the chemical industry.

The simplest utilization method of crude glycerol is its combustion, which is an advantageous method as it does not require any purification. However, this process is not easy from a technological point of view. The heat of combustion is about half of that of fossil fuels, it is highly viscous, making it difficult to spray, and it has a high auto-ignition temperature (about 370 °C). Also, low temperatures of burning can generally produce acrolein (between 280 and 300 °C). The presence of mineral salts causes corrosion problems in the burner nozzles and in the combustion system itself, which also act as inhibitors of the flame, which makes combustion of crude glycerol very difficult.

The glycerin market is a complex, volatile market which is dependent on global supply. There have been many changes in the glycerin market over the last twenty years, making it difficult to develop a model to predict future prices. The price of domestic refined glycerin is negatively correlated with Middle Eastern petroleum production and European glycerin production.

Global glycerin production has increased dramatically in recent years due to renewable fuel production driven by subsidies, tax breaks, and usage mandates. Prices have dropped due to the increased supply of glycerin. Refined glycerin prices have almost halved while crude prices hover between five and fifteen cents a pound.

Biodiesel production is inadvertently affecting the soap manufacturing and fatty acid production industries by competing for input feedstock and driving down glycerin prices. This probably will make some of these companies move their operations abroad. Since most of the country's refineries are owned by the manufacturers of fatty acid and soap, this could cause a decrease in refined glycerin capacity.

Coinciding with most data published in the scientific literature, burning of crude glycerol can contribute to reduce the countries' dependence on imported petroleum. It is renewable and it contributes less to global warming, unlike petroleum fuels, because of its closed carbon cycle. The main raw material can grow season after season and most of the carbon in the fuel was originally removed from the atmosphere by the plant. Finally, today, crude glycerol has a low cost.

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